

1 Patent Application of

Bor Z. Jang

for

**PHOTO-ELECTROLYTIC CATALYST SYSTEMS AND METHOD FOR  
HYDROGEN PRODUCTION FROM WATER**

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**FIELD OF THE INVENTION**

This invention provides a photo-electrolytic catalyst system for water splitting to produce hydrogen and oxygen gases. This invention also provides a method of using an improved semiconductor-based photo-electrolytic catalyst to promote solar energy conversion of water or aqueous electrolyte into hydrogen.

11  
**BACKGROUND OF THE INVENTION**

A fuel cell converts chemical energy into electrical energy and some thermal energy by means of a chemical reaction between hydrogen-containing fuel and oxygen. As compared to other energy sources, fuel cells provide advantages that include low pollution, high efficiency, high energy density and simple fuel recharge. Fuel cells can be used in electrochemical engines, portable power supplies for various microelectronic and communication devices, standby power supply facilities, power generating systems, etc. Further, fuel cells utilize renewable resources and provide an alternative to burning fossil fuels to generate power.

21 For fuel cell applications, hydrogen is the "ultimate fuel." Hydrogen is practically inexhaustible since it is the most plentiful element in the universe (over 95% of all matter). Furthermore, hydrogen is an inherently low cost fuel. Hydrogen has the highest energy density per unit weight of any chemical fuel and is essentially non-polluting since the main by-product of "burning" hydrogen is water. Thus, hydrogen can be a means of solving many of the world's energy related problems, such as global warming, pollution, strategic dependency on oil, etc. Hydrogen can be produced by various processes which split water into hydrogen and oxygen or which oxidize methanol or ethanol into hydrogen and other molecules. The hydrogen can then be stored and transported in a solid state form.

1 Hydrogen is produced as a co-product in various industrial processes. For example,  
hydrogen is produced as a co-product in the electrolysis of aqueous alkali metal halide brines to  
yield the corresponding alkali metal hydroxide, the halogen, and hydrogen. Hydrogen is also  
produced as a co-product in the electrolysis of aqueous alkali metal sulfates to yield the alkali  
metal hydroxide, oxygen, and hydrogen. In all of these industrial processes, electrical power  
6 must be applied from an external power supply, across an anode and a cathode of an electrolytic  
cell, to yield oxygen or halogen at the anode, the alkali metal hydroxide at the cathode, and  
hydrogen as a cathode co-product.

11 The photolysis of water into  $H_2$  and  $O_2$  using solar radiation is an attractive method of  
producing hydrogen since it involves renewable and non-polluting energy sources: water and  
sunlight. The conversion of solar energy into chemical energy has the advantage of easy energy  
storage (in the form of the photo-generated fuel), as compared with solar energy conversion via  
photovoltaic or photo-thermal processes. An important process for accomplishing the  
decomposition of water into  $H_2$  and  $O_2$  using solar radiation is photo-electrolysis.

16 Photo-electrolytic decomposition of water using a pair of n-type and p-type  
semiconductor electrodes electrically connected by an electrolyte solution was disclosed by  
Tchernev in U.S. Pat. No. 3,925,212 (Dec. 9, 1975). Nozik (U.S. Pat. No. 4,094,751, June 13,  
1978) disclosed photochemical diodes which use light to drive both endoergic and exoergic  
21 chemical reactions such that optical energy is converted into chemical energy. Either Schottky-  
type (rectifying metal-semiconductor junction) or p-n type diodes were employed to convert  
water into hydrogen and oxygen gases. In a typical photochemical diode, for instance, the p-type  
portion and the n-type portion are intimately joined together through an ohmic contact. Gratzel,  
et al. (U.S. Pat. No. 4,389,290, June 21, 1983) disclosed a photolytic system comprising a  
26 darkened half cell and an illuminated half cell in which oxidation and reduction are made to  
occur. Ayers (U.S. Pat. No. 4,466,869, Aug. 21, 1984) developed a multi-layered photo-  
electrolytic device to produce hydrogen. This complicated device includes a multiplicity of  
stacked photoelectric or photovoltaic elements between a substrate and an electrode, a counter-  
electrode, and an unbiased external circuit. Another complicated, multi-layer photo-electrolytic

1 device is disclosed by Gordon (U.S. Pat. No. 4,650,554, March 17, 1987).

Photolytic decomposition of water was also accomplished by Khan, et al. (U.S. Pat. No. 4,889,604, Dec. 26, 1989) who used a catalyst system that included a semiconductor of hexagonal crystal structure loaded with a noble metal and a transition metal oxide. The catalyst was suspended in ethylene diamine tetra-acetic acid (EDTA) as a part of the catalyst system. The photo-catalytic method for water decomposition disclosed by Sayama, et al. (U.S. Pat. No. 5,262,023, Nov. 16, 1993) involved bringing an aqueous solution of carbonate into contact with a semiconductor carrying a metal or a metal compound, and irradiating the aqueous solution with light. The photo-catalyst used by Takaoka, et al. (U.S. Pat. No. 5,759,948, June 2, 1998) was composed of titanium oxide particles which have part or the whole of an iron compound supported thereon. A series of photo-catalysts each consisting of a catalytically active ingredient (e.g., Cs and CdS) and a supporting or promoting ingredient (e.g., Ni, Co, Fe, and  $K_4Nb_6O_{17}$ ) were proposed by Park and co-workers (U.S. Pat. No. 5,865,960, Feb. 2, 1999; No. 6,017,425, June 25, 2000; No. 6,077,497, June 20, 2000; No. 6,300,274, Oct. 9, 2001; No. 6,297,190, Oct. 2, 2001; U.S. Appl. No. 09/735,605, filed Dec. 14, 2000). Bipolar electrodes with a semiconductor coating, titanium dioxide doped with iron, was disclosed by Haug, et al. (U.S. Pat. Appl. No. 09/783,228, filed Feb. 14, 2001).

The above inventions have one or several of the following drawbacks: (1) complicated junctions or multiple-layer structures, (2) insufficient photolytic or photo-electrolytic efficiency, (3) slow hydrogen production rate, (4) involving non-water liquid ingredients (e.g., EDTA, acid, strong base, or other potentially hazardous chemicals), and (5) photo-catalysts with unknown operating mechanisms (hence, the resulting efficiency, yield, and rate can only be improved by trial-and-error and cannot be readily or effectively optimized).

## SUMMARY OF THE INVENTION

This invention provides simple (non-complicated) but effective photo-electrolytic catalyst systems which comprise two materials: (a) a semiconductor material with a non-zero energy gap  $E_g$  which, in response to an incident radiation having an energy greater than  $E_g$ ,

1 generates electron-hole pairs as charge carriers; and (b) a facilitating material in electronic  
contact with the semiconductor material to facilitate separation of the radiation-generated  
electrons from the holes to reduce the probability of charge carrier recombinations. The catalysts  
make use of both majority and minority charge carriers to promote photo-electrolysis reactions  
for producing hydrogen at higher rates and improved efficiencies.

6 The semiconductor material and/or the facilitating material preferably has at least one  
dimension being smaller than one micron ( $1\text{ }\mu\text{m}$ ) and, further preferably, smaller than or equal to  
100 nm. Either or both materials are preferably porous. These two features (small dimensions  
and high porosity levels) more readily facilitate the separation of the photon-generated electrons  
11 and holes and provide larger material-water interface areas where redox reactions occur, leading  
to more efficient and faster hydrogen production.

The present invention also provides a method of using these photo-electrolytic catalysts to  
generate hydrogen gas from water.

## 16 **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG.1 (A) Upward bending of energy band curves for an n-type semiconductor and (B)  
Downward bending of energy band curves for a p-type semiconductor.

FIG.2 (A) Upward bending of energy band curves for an n-type semiconductor at a rectifying  
21 contact interface and (B) Downward bending of energy band curves for a p-type  
semiconductor at a rectifying contact interface.

FIG.3 (A) Upward bending of energy band curves for an n-type semiconductor at a rectifying  
semiconductor-electrolyte contact interface and downward bending at a semiconductor-  
facilitating material interface and (B) Downward bending of energy band curves for a p-  
26 type semiconductor at a rectifying semiconductor-electrolyte contact interface and upward  
bending at a semiconductor-facilitating material interface.

## **DETAILED DESCRIPTION OF THE INVENTION**

### **A. Basic Operating Mechanisms of the Invented Photo-electrolysis Catalyst Systems**

1 In conventional photo-electrolysis, light is absorbed in separate, discrete semiconducting  
electrodes in contact with an electrolyte. Ideally, the absorbed light generates electron-hole pairs  
within the electrodes which, hopefully, are subsequently separated by the semiconductor-  
electrolyte junctions. At the cathode and anode, electrons and holes are respectively injected into  
the electrolyte, thereby inducing reduction and oxidation reactions, respectively. Electrons and  
6 holes are known to be strong reducing and oxidizing agents, respectively. Hence, an overall  
photo-electrolysis reaction is achieved in two steps: (1) electrons and holes are first generated by  
photo-excitation of electrons across an energy band gap ( $E_g$ ) of a semiconducting electrode, and  
(2) the electrons and holes drive chemical reactions in either or both electrodes. In such a photo-  
chemical process, the possibility exists that this sequence can drive reactions at more favorable  
11 energies than can either *direct photolysis* or *direct electrolysis* acting independently.

In order for such a photo-electrolysis process to work efficiently, the electrons and holes  
generated must be immediately separated, at least tentatively, from each other to reduce or  
eliminate electron-hole charge recombinations. In a conventional Schottky-type photo-  
16 electrolysis cell (e.g., as disclosed in U.S. Pat. No. 3,925,212), the semiconductor/ohmic contact  
forms one electrode, while metal forms the second, or counter-electrode. The two electrodes are  
separated by the electrolyte, being joined externally by an electrical circuit to provide a path for  
hole and electron transfer, possibly as a means of separating electrons from holes. In a  
conventional p-n type photo-electrolysis cell, the p-type semiconductor/ohmic contact forms one  
21 electrode, while the n-type semiconductor/ohmic contact forms the other electrode. Again, the  
two electrodes are separated by the electrolyte and are joined externally by an electrical circuit to  
provide a path for electron and hole transfer.

26 In an improved photo-electrolysis system (Nozik, U.S. Pat. No. 4,094,751), either  
Schottky-type or p-n type photo-chemical diodes were employed to convert water into hydrogen  
and oxygen gases. Each diode comprises two portions, e.g., in the case of a p-n type diode, the p-  
type portion provided with an ohmic contact and the n-type portion also provided with an ohmic  
contact. The two portions are intimately joined or bonded together through the ohmic contacts.  
The conventional wisdom maintains that, for a p-n photo-chemical diode, the ohmic contact

1 permits recombination of the photo-generated majority carriers in the respective regions of the diode, and thereby allows the minority carriers to be injected into the electrolyte to complete the current path. That is, the photons absorbed in each portion of the p-n photochemical diode create electron-hole pairs; the minority holes (from the n-type portion) and the minority electrons (from the p-type portion) are injected into the electrolyte. The majority electrons and holes must  
6 recombine for current continuity to exist, and this can only happen if ohmic contacts are sandwiched between the p- and n-type semiconducting portions of the diode. Such a concept has a serious drawback in that the majority charge carriers (that normally outnumber the minority charge carriers by several orders of magnitude) are all wasted, not given an opportunity to catalyze the respective oxidation and reduction reactions in an aqueous medium.

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Contrary to the teachings of the prior art and in accordance with the present invention, photo-electrolytic catalyst systems are provided which comprise two materials: (a) a semiconductor material with a non-zero energy gap  $E_g$  which, in response to an incident radiation having an energy greater than  $E_g$ , generates electron-hole pairs as charge carriers; and  
16 (b) a facilitating material in electronic contact with the semiconductor material to facilitate separation of the radiation-generated electrons from the holes to reduce the probability of charge carrier recombinations. Such a new photo-electrolysis catalyst system, preferably in the form of a fine powder or a micron- or sub-micron-scale entity, may simply be suspended or dispersed in an aqueous electrolyte. Preferably, the facilitating material has a high surface-to-volume ratio, thus providing a large surface area whereon majority charge carriers can tentatively reside prior  
21 to catalyzing respective reduction and oxidation reactions at the facilitating material-electrolyte (water) interfaces. In addition to the majority charge carriers being capable of catalyzing the chemical reactions, minority charge carriers are capable of being directly injected into the aqueous medium to complete the current path as well as catalyzing the redox reactions.

26  
The need to have a high surface-to-volume ratio can be achieved by making the catalyst system in small scales or of high porosity. The facilitating material and/or the semiconductor material preferably are (is) micron-scaled and further preferably nano-scaled ( $< 100$  nm). The facilitating material is preferably micro-porous or nano-porous, with a large number of micron-

1 or nano-scale pores to accommodate water molecules and to allow the resulting hydrogen and oxygen molecules to escape. These large surface areas provide large facilitating material-water interfaces where reduction/oxidation reactions occur. The present invention also eliminates the need for both large planar electrode systems and external circuitry.

6 The hole-electron separation-facilitating material preferably has an attribute in that it can tentatively retain majority charge carriers (e.g., electrons) therein or thereon to give the retained charge carriers improved chances of encountering reactant species and reacting therewith (e.g.,  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  or  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$ ). For an n-type semiconductor, the facilitating material may preferably comprise a reduction catalyst such as platinum (Pt). For a p-type  
11 semiconductor, the facilitating material may preferably comprise an oxidation catalyst such as ruthenium oxide ( $\text{RuO}_2$ ). Although these features are preferred, they are not necessary requirements. For an intrinsic semiconductor, either type or both types of catalysts may be used as a facilitating material.

## 16 **B. The Constituent Semiconductor Material**

For the purpose of clearly defining the claims, the term semiconductor refers to a single element-type material such as silicon (Si) or a multiple-element material such as gallium arsenide (GaAs) provided that it has non-zero energy band gap ( $E_g$ ). A multiple-element semiconductor typically contains at least one metal element. In the present context, any conventionally defined  
21 “electrical insulator” such as oxides, nitrides and carbides (despite having a large energy gap, e.g.,  $E_g$  greater than 3.0 eV) will be considered as a semiconductor. A “metal” refers to an element of Groups 2 through 13, inclusive, plus selected elements in Groups 14 and 15 of the periodic table. Thus, the term “metal” broadly refers to the following elements:

Group 2 or IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

26 Groups 3-12: transition metals (Groups IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB), including scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc),

- 1 hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and mercury (Hg).
- 6
- Group 13 or IIIA: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).
- Lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).
- 11
- Group 14 or IVA: germanium (Ge), tin (Sn), and lead (Pb).
- Group 15 or VA: antimony (Sb) and bismuth (Bi).

16 For photo-electrolysis catalyst applications, the metal is preferably selected from the group consisting of aluminum, antimony, bismuth, boron, cadmium, copper, iron, gallium, germanium, indium, lead, titanium, tin, and zinc. Preferably a counter ion element is selected from the group consisting of hydrogen, oxygen, carbon, nitrogen, chlorine, fluorine, boron, iodine, sulfur, phosphorus, arsenic, selenium, tellurium and combinations thereof. These elements may be used to react with a metal to form a compound or ceramic of hydride, oxide, carbide, nitride, chloride, fluoride, boride, iodide, sulfide, phosphide, arsenide, selenide, and telluride, and combinations thereof. The range of compound semiconductor or ceramic materials that can be used as a semiconductor includes, but not limited to, I-VII, II-VI, and III-V compounds. All of these materials can be selectively doped with electron-donors or electron acceptors to produce n-type or p-type semiconductors. Pure, un-doped semiconductors are referred to as intrinsic semiconductors. Table 2 shows some of the preferred semiconductors for use in the invented photo-electrolysis catalyst.

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Table 1. Selected semiconductor materials.

	n-type	p-type
	<u>Miscellaneous</u>	
6	TiO <sub>2</sub>	Cu <sub>2</sub> O
	CoO	CuS
	NiO	
	M <sub>x</sub> Zn <sub>y</sub> O <sub>2</sub>	
	MTiO <sub>3</sub>	
	ZnO	
11	Fe <sub>2</sub> O <sub>3</sub>	
	WO <sub>3</sub>	
	Si, Te, SiC	Si, Ge, SiC
	(M is a transition metal element or rare-earth metal element)	
	<u>II-VI compounds</u>	
16	CdS	CdTe
	CdSe	ZnTe
	CdTe	ZnSe
	<u>III-V compounds</u>	
21	GaP	GaP
	GaAs	GaAs
	InP	InAs
	AlAs	AlAs
	AlSb	AlSb
	GaSb	GaSb
26	InP	
	<u>Mixed crystals of II-VI compounds</u>	
	Cd <sub>1-x</sub> Zn <sub>x</sub> S	
	<u>Mixed crystals of III-V compounds</u>	
31	GaAs <sub>x</sub> P <sub>1-x</sub>	GaInP <sub>2</sub>
	Cu <sub>x</sub> In <sub>y</sub> Ga <sub>z</sub> Se <sub>2</sub>	
	GaIn <sub>1-x</sub> As	
	Al <sub>x</sub> Ga <sub>1-x</sub> As	
	Chalcopyrites	Chalcopyrites
	Chalcogenides	Chalcogenides
36	<u>I-III-V<sub>2</sub> compounds</u>	
	CuInS <sub>2</sub>	CuInS <sub>2</sub>
	AgInSe <sub>2</sub>	CuGaS <sub>2</sub>
	AgInS <sub>2</sub>	CuAlS <sub>2</sub>
41	CuInSe <sub>2</sub>	CuAlSe <sub>2</sub>
		CuInSe <sub>2</sub>
	<u>II-IV-V<sub>2</sub> compounds</u>	
	ZnSiP <sub>2</sub>	ZnSiAs <sub>2</sub>
	CdSiP <sub>2</sub>	ZnGeP <sub>2</sub>

1	CdSnP <sub>2</sub>	ZnSnAs <sub>2</sub>
	CdSnAs <sub>2</sub>	ZnSnP <sub>2</sub>
		ZnSnSb <sub>2</sub>
		CdSnP <sub>2</sub>
		CdSnAs <sub>2</sub>
6	<u>ZMO compounds (Z = alkaline or alkali metal)</u>	
	K <sub>4</sub> Nb <sub>6</sub> O <sub>17</sub>	
	Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	
	K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	
	<u>BaTi<sub>4</sub>O<sub>9</sub></u>	

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### C. Electron-Hole Separation-Facilitating Materials

If a semiconductor is in a physical contact with a metal, a rectifying contact (Schottky junction) or an ohmic contact is formed, depending on the type of metal used. Assume that the surface of an n-type semiconductor has somehow been negatively charged, as schematically shown in FIG. 1A. The negative charges repel the free electrons that had been near the surface and leave positively charged donor ions behind (e.g., As<sup>+</sup>). Any electron which drifts toward the surface (i.e., moving in the negative X-direction toward the surface) “feels” this repelling force. As a consequence, the region near the surface has less free electrons than the interior of the solid. This region is known as the depletion layer or space charge region. The repelling force of an external negative charge may be customarily represented by an upward-bending energy band curve near the surface, FIG. 1A. This implies that the electrons like to roll downhill. Similarly, if a p-type semiconductor is somehow positively charged at the surface, the positive charge carriers (holes) are repelled toward the inert part of the material and the band edges are bent downward, FIG. 1B. This represents a potential barrier for holes because the holes have to drift upward in order to come closer toward the surface.

Assume that a metal with a work function  $\phi_M$  is brought into contact with an n-type semiconductor with a work function  $\phi_n$ , where  $\phi_M > \phi_n$ , electrons start to flow from the semiconductor “down” into the metal until the Fermi energies of both materials are equal. As a consequence, the metal will be charged negatively and a potential barrier is formed just as shown in FIG. 1A. This means that the energy bands in the bulk semiconductor are lowered by the amount  $(\phi_M - \phi_n)$  with respect to a point A at the metal-semiconductor interface, FIG. 2A

1 Such a junction is a rectifying contact. Contrarily, if  $\phi_M < \phi_n$ , the contact will be an ohmic  
contact and the energy band curves near the metal-semiconductor interface will be down-ward  
bending.

6 Similarly, if a p-type semiconductor (work function  $\phi_p$ ) is brought into contact with a  
metal and  $\phi_M < \phi_p$ , electrons diffuse from the metal into the semiconductor and, therefore, the  
surface of the p-type semiconductor is charged positively. A potential barrier ( $\phi_p > \phi_M$ ) is  
formed just as shown in FIG.1B. This situation is illustrated by a “downward” potential barrier  
(for the hole), indicated in FIG.2B. Contrarily, if  $\phi_M > \phi_p$ , the contact will be an ohmic contact  
and the energy band curves near the metal-semiconductor interface will be up-ward bending.  
11 When a p-type semiconductor and an-n-type semiconductor are brought into contact with each  
other, a rectifying potential barrier is established.

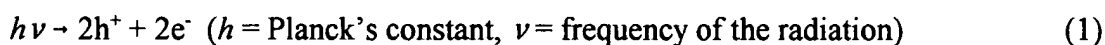
The interface between a liquid electrolyte (e.g., water) and a semiconductor is similar to  
a metal-semiconductor junction and can be an ohmic contact or a rectifying contact, depending  
16 upon the relative magnitudes of the work functions as explained above, using FIGs. 1A, 1B, 2A,  
and 2B. With an n-type ZnO ( $E_g = 3.35$  eV) as an example, photo-chemical splitting of water at  
the water-ZnO interface and the direct conversion of solar energy into chemical energy may be  
represented as a process in the rectifying metal-semiconductor junction (e.g., at interface A of  
FIG.3A) or in one half of a p-n junction. When solar radiation is absorbed in the n-type ZnO,  
21 electron-hole pairs are created. The potential gradient established at the depletion zone forces  
the electrons to drift into the bulk of the semiconductor and likely become wasted (not  
participating in any chemical reactions). However, the holes drift to the surface of the  
semiconductor where they may combine with  $\text{HO}^-$  ions or react with  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}^+ +$   
 $\frac{1}{2}\text{O}_2$ ) and result in the evolution of oxygen gas.

26 The present invention provides a facilitating material that “attracts” the photo-generated  
electrons or promotes the photo-generated electrons to sweep across the “bulk” of the n-type  
semiconductor and across the facilitating material-semiconductor interface (e.g., interface B of  
FIG.3A) so that they have opportunities to combine with  $\text{H}^+$  or react with  $\text{H}_2\text{O}$  at the facilitating

material-electrolyte interface to produce hydrogen (e.g., through  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$ ). Without the presence of this facilitating material, these electrons would somehow recombine with the defects or holes in the bulk of the semiconductor and would be wasted. In one preferred embodiment, the semiconductor has one dimension smaller than  $1\text{ }\mu\text{m}$  and further preferably has one dimension smaller than 100 nanometers (nm). Preferably, the facilitating material also has a dimension smaller than  $1\text{ }\mu\text{m}$  and, further preferably, smaller than 100 nm. Alternatively or additionally, the facilitating material and/or the semiconductor material is porous, being meso-porous (pore size  $> 10\text{ }\mu\text{m}$ ), micro-porous ( $0.1\text{ }\mu\text{m} < \text{pore size} < 10\text{ }\mu\text{m}$ ), and/or nano-porous (pore size  $< 0.1\text{ }\mu\text{m}$ ). The small dimension(s) of the semiconductor make it easier for the photo-generated charges to readily sweep across the bulk of the semiconductor (the “bulk” itself being so small) with reduced chances of recombinations. A porous semiconductor means a larger surface area to promote hole-water contacts. Both the small dimension(s) and the pores of the facilitating material mean greater interface areas between the facilitating material and water where desirable hydrogen production reactions can occur.

In the case of a p-type semiconductor (e.g., an acceptor-doped ZnSe), the corresponding process involves the generation of hole-electron pairs by the absorption of solar radiation. The electrons in this case are forced to drift to the surface while the holes drift to the bulk of the semiconductor. At the semiconductor-water interface (e.g., interface A of FIG.3B), the electrons are transferred to the electrolyte where they combine with  $\text{H}^+$  and cause the evolution of hydrogen. Without the assistance of a facilitating material, the holes would somehow disappear in the bulk through undesired recombinations and would not assist in the water splitting reactions. The facilitating material “attracts” the photo-generated electrons or promotes the photo-generated holes to sweep across the “bulk” of the p-type semiconductor and across the facilitating material-semiconductor interface (e.g., interface B of FIG.3B) so that they have opportunities to combine with  $\text{OH}^-$  or react with  $\text{H}_2\text{O}$  at the facilitating material-electrolyte interface to produce oxygen and hydrogen ion (e.g., through  $\text{H}_2\text{O} + 2\text{h}^+ \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 \uparrow$ ).

The overall photoelectro-catalytic splitting of water may be conveniently expressed as:





However, from the perspective of reaction mechanisms, the overall reaction may begin with electrolysis of water:



6                    The required water redox potential ( $\Delta E \approx 1.23 \text{ eV}$ ) may come from the semiconductor, the facilitating material, or a combination. The resulting ions of  $\text{OH}^-$  and  $\text{H}^+$  may then react with holes and electrons to produce oxygen and hydrogen, respectively:



11                   It is important to realize that both electrons and holes are essential to completing the above loop of reactions (Eqn.(2)-(6)). Even though one may be interested in collecting hydrogen only, the production of oxygen is indispensable because the production of oxygen (Eqn.(2) or Eqn.(5)) also results in the formation of  $\text{H}^+$  ions as a co-product, which is needed for hydrogen production to complete the loop. This is another reason why a facilitating material is desired in the invented photo-electrolytic catalyst system. Further, a small amount of energy is lost to heat and other loss mechanisms and, hence, a potential greater than 1.23 eV (typically  $> 1.6 \text{ eV}$ ) is required for electrolysis of water. Therefore, a semiconductor with a band gap greater than 1.6 eV is preferred.

21                   The facilitating material may include an element selected from Group VI and Group VII of the Periodic Table of Elements. The facilitating material may include a transition metal element or a rare earth element. Preferably, the facilitating material may include an element selected from the group consisting of Fe, Mn, Co, Ni, Cr, and Ti. The above elements were found to constitute very effective facilitating materials.

26                   In order to make better use of the solar radiations, it is advantageous to combine or mix two or three semiconductor materials together that share with the same facilitating material to form a hybrid photo-electrolytic catalyst system. The two or three semiconductors are preferably of different energy band gaps, covering both UV and visible wavelengths. A semiconductor

1 material or a hybrid combination of two or three semiconductor materials may be in electronic  
contact with two or more facilitating materials. Preferably, one facilitating material is an  
electron-drawing material while another one is a hole-drawing material. Such a combination  
could more effectively facilitate the separation of electrons from holes immediately after they  
are photo-generated in a semiconductor. When three or more semiconductor materials are  
6 combined, they are preferably connected electrically in series. The resulting solid state junctions  
at the micro- or nano-scale act to reduce semiconductor-electrolyte interface voltage  
requirements.

Another preferred embodiment of the present invention is a method for producing  
11 hydrogen from water or an aqueous electrolyte. The method comprises suspending photo-  
electrolytic catalysts as illustrated above in an aqueous electrolyte (including, but not limited to,  
pure water or sea water) and then illuminating the catalysts with optical energy. The method  
may further include means of collecting the hydrogen gas produced.

#### 16 Example 1.

A micro-crystalline powder of GaP (average particle size  $\approx 0.7 \mu\text{m}$ ) was doped with  
sulfur to produce an n-type semiconductor. A thin layer of platinum (Pt) was sputter-coated over  
a portion of individual n-GaP particles to serve as a facilitating material. When such a photo-  
electrolytic catalyst system was suspended in an aqueous solution, hydrogen was evolved.

#### 21 Example 2.

Materials similar to those in Example 1 were used, but the average particle size of GaP  
was slightly below 100 nm. When such a photo-electrolytic catalyst system was suspended in the  
same aqueous solution, hydrogen was much more vigorously evolved.

#### 26 Example 3.

Several samples were prepared for this example. As in Example 2, nano-scaled n-type  
GaP powder was used, but the facilitating materials were Mn, Fe, Ni, and Co, respectively.  
When such photo-electrolytic catalyst systems were suspended in the same aqueous solution,

hydrogen was vigorously evolved. The solar-to-hydrogen power conversion efficiencies for these samples were found to be in the following order: Mn ≈ Fe > Ni > Co (as facilitating materials).

#### Example 4.

Several samples were prepared for this example. As in Example 3, nano-scaled p-type ZnTe powder was used and the facilitating materials were Mn, Fe, Ni, and Co, respectively. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was vigorously evolved. The solar-to-hydrogen power conversion efficiencies for these samples were found to be in the following order: Mn ≈ Fe > Ni > Co (as facilitating materials). The efficiencies are slightly lower than those of corresponding catalysts using n-type GaP as the semiconductor material

#### Example 5.

Several samples were prepared for this example. Nano-scaled n-type ZnO powder was used, but the facilitating materials were RuO<sub>2</sub>, IrO<sub>2</sub>, and NiO, respectively. The three oxides are well-known oxidation catalysts. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was vigorously evolved.

#### Example 6.

Three samples were prepared for this example. As in Example 2, nano-scaled n-type GaP powder was used, but the facilitating materials, MnO, Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, respectively, were deposited via reactive sputtering. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was more vigorously evolved in the samples containing Mn<sub>3</sub>O<sub>4</sub> or Mn<sub>2</sub>O<sub>3</sub> than in that containing MnO as the facilitating material. This may be understood from the fact that polyvalent ions (such as Mn<sup>3+</sup>) are more powerful electron-drawing materials than a divalent Mn<sup>2+</sup>. Furthermore, with a polyvalent ion, reactions similar to the following may occur:



The present invention provides photo-electrolytic catalysts that are efficient in un-biased water splitting for hydrogen production. No external circuit or electric power is needed, the only energy source is solar radiation or other forms of light. No complex solid state microelectronic devices (such as multi-layer thin-film junctions) are needed.